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International Classification:—**C08b, g, j. H01m.**

COMPLETE SPECIFICATION

Improvements relating to Inter-Electrode Separators for Electric Cells

We, IONS EXCHANGE & CHEMICAL CORP., a corporation organised under the laws of the State of New York, United States of America, of 48 Leonard Street, New York 13, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to inter-electrode separators for electric cells and is particularly although not exclusively concerned with such separators for batteries or accumulators of the alkaline type in which the electrodes are closely confined in a casing and are applied under pressure against semi-permeable membranes.

Among the materials heretofore proposed for such separators is polyvinyl alcohol but it has been found that as the standards of performance for alkaline batteries are raised, known separator materials no longer meet all requirements concerning mechanical and electrical strength, electrical characteristics and length of service life. The general object of the present invention is, accordingly, to provide an improved separator material which will better withstand penetration by minute particles of active negative electrode material (for example zinc in the case of a silver-zinc cell) and/or will have greater ability to resist attack by a strong oxidising agent participating in the electrochemical reaction (for example silver peroxide in the case of a silver-zinc cell) while at the same time exhibiting the low electrolyte resistance necessary for high-capacity batteries.

According to the present invention a semi-permeable separator for the electrodes of an electric cell comprises a sheet formed of a mixture of a polyvinyl compound and a different film-forming water-insoluble organic polymer acting as a protective agent.

The polyvinyl compound preferably comprises polyvinyl alcohol (PVA) and/or a polyvinyl-methyl-ether/maleic-acid copolymer (PVM/MA), admixing with a film-forming substance specifically adapted to protect the mixture against the afore-mentioned penetration and/or oxidation.

More specifically, the protective substance admixed with the polyvinyl compound may be a film-forming, water-insoluble polymer derived from a monomer with at least three carbon atoms, at least two oxygen atoms and not more than two nitrogen atoms. This group comprises the polyacrylates, such as methyl methacrylate polymer $[—CH_2CH—CH—COOCH_3—]n$, polyamides (nylon) $[—HN—CO—(CH_2)_4—CO—NH—(CH_2)_6—NH—]n$, and methyl cellulose $[—(C_6H_{10}O_4)—O—]n$.

Films produced from the foregoing substances, embodying the present invention, are distinguished by their freedom from pinholes, evidenced by substantially complete air impenetrability, and by their ability to adhere firmly to a supporting base, such as, for example, a nylon fabric. If high tensile strength is not a major requirement, they can also be used as self-supporting films produced by casting their liquid phase upon a glass surface or the like.

The film-forming ability of the materials embodying the invention can be further improved, if desired, by the admixture of plasticisers, such as, for example, glycerol or glycols. In order to make the resulting film more resistant to oxidation, a limited amount of antioxidant may be incorporated therein; a suitable anti-oxidant is N-(*p*-hydroxyphenyl) morpholine, marketed under the trade name "Solux".

[*Price 3s. 6d.*]

Price 25p

EXAMPLE I.

A viscous liquid is prepared by mixing together the following ingredients:—

100 grams of an aqueous solution of 5—10% by weight of methyl cellulose;
100 grams of an aqueous solution of 8—12% by weight of PVM/MA;
30—50 grams of a 10% aqueous PVA solution;
up to 6 grams of diethylene glycol;
0.1 gram of " Solux ".

The mixture is applied to a permeable backing, such as a nylon fabric, by dipping, calendering, knife coating or spraying, and is then dried in air or in an oven, or is cast on a non-adhering support (e.g. glass) and stripped off after drying.

It will be noted that the ratio of methyl cellulose solids to polyvinyl solids (PVA plus PVM/MA) can be varied between roughly, 1:3 and 1:1, although it may be mentioned that for some applications these limits may be exceeded. Thus, it has been found that at ratios smaller than 1:3 there may occur objectionable zinc penetration (in a silver-zinc cell), whereas at ratios greater than 1:1 the electrolytic resistance of the film rises rather rapidly beyond a value of about 0.3 ohms/cm^2/mm which it reaches in the neighbourhood of the 1:1 ratio. Also, the proportion of anti-oxidant (" Solux ") should preferably not exceed about double the amount indicated in the example, since otherwise the capacity of the cell may suffer by reason of a reduction of the active material of the positive electrodes.

EXAMPLE II.

The following ingredients are mixed together:—

200 grams of an acrylic resin, suspended as an emulsion in 100 grams of water, e.g. an emulsion of this character marketed under the trade name " Rhoplex ";
100—200 grams of a 10% aqueous PVA solution.

This mixture can be used as a coating or cast into a self-supporting film in the manner described in Example I.

Again, the limits given in the example may be exceeded in some instances, although it will usually be observed that beyond the stated upper limit of the acrylate-PVA ratio (2:1) the electrolytic resistance rises rapidly above a value of 0.25 ohms-cm^2/mm which it reaches in the neighbourhood of that ratio, whereas at ratios below the stated lower limit of 1:1, the oxidation resistance of the film may be inadequate.

EXAMPLE III.

A mixture is prepared from the following ingredients:—

100 grams of a 10% solution, in ethyl or isopropyl alcohol, of a short-chain, water-insoluble nylon resin, e.g. an alcohol-soluble powder marketed under the trade name " Zytel ";
100 grams of a 10% PVM/MA solution in ethyl or isopropyl alcohol.

The last example gives a lower limit of 2:3 and an upper limit of 1:1 for the nylon-PVM/MA ratio, these limits arising from considerations similar to those set forth in connection with Example II and being subject to change for particular applications. It is to be noted, moreover, that useful mixtures for the purpose indicated may be obtained by interchanging the protective agents and the polyvinyl compounds of the several examples given hereinabove, and that a value of the order of 1:1 for the ratio of protective agent versus polyvinyl compound will again be satisfactory, in most instances, in the case of the films so produced.

The substance according to the invention may form coatings of a thickness as little as 0.01 mm without apparent air permeability; since nylon fabrics are at present available in thicknesses as low as 0.05 mm, it is possible by the processes herein disclosed to produce a separator of satisfactory tensile strength, free from pinholes, resistant to oxidation and virtually impervious to harmful ions with a thickness well below 0.1 mm.

WHAT WE CLAIM IS:—

1. A semi-permeable separator for the electrodes of an electric cell comprising a sheet formed of a mixture of a polyvinyl compound and a different film-forming water-insoluble organic polymer acting as a protective agent.

2. A separator according to Claim 1 in which the polymer is derived from a monomer with at least three carbon atoms, at least two oxygen atoms and not more than two nitrogen atoms.

3. A semi-permeable separator according to any one of the preceding claims in which the protective agent is selected from the group which consists of polyacrylates, polyamides and methyl cellulose.

4. A semi-permeable separator according to any one of the preceding claims in which the polyvinyl compound is selected from the group which consists of polyvinyl alcohol and polyvinyl-methyl-ether/maleic-acid copolymer.

5. A material according to Claim 4, wherein the ratio of said compound to said agent is of the order of 1:1.

6. A separator according to any one of the preceding claims in which said sheet forms a coating on a permeable support.

7. A separator according to Claim 6 in which the support is flexible and perforated.

8. A separator according to Claim 6 or Claim 7 in which the support is of sheet material.

9. A separator according to Claim 8 in which the sheet is of non-cellulosic material.

10. A separator according to any one of Claims 6 to 9 in which the support is of fabric material.

11. A separator according to any one of

Claims 6 to 10 in which the support is a web of non-cellulosic fibres.

12. A separator according to any one of Claims 6 to 11 in which the support is of nylon mesh.

13. A separator according to any one of Claims 6 to 12 in which the combined thickness of the support and the coating is of the order of not more than 0.1 mm.

14. A separator for the electrodes of an electric cell substantially as herein described.

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